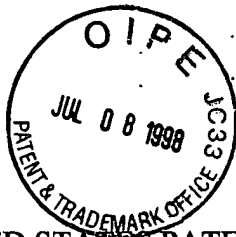


NASA Docket No. LEW 16183-1



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Patent  
JUL 17 1998  
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In re application of )

DellaCorte, et al. )

Serial No. 08/786,360 )

Filed January 16, 1997 )

SELF-LUBRICATING COMPOSITE )  
CONTAINING CHROMIUM OXIDE )

Art Unit 1721

Examiner: Cephia D. Toomer

Honorable Commissioner of Patents and Trademarks  
Washington, DC 20231

Sir:

DECLARATION UNDER 37 CFR 1.132

Christopher DellaCorte, residing at 7036 Beach Road, Medina, Ohio 44256 declares:

That, he is one of the inventors of the invention disclosed and claimed in the above-identified application;

That, he holds a PhD degree with a major in Mechanical Engineering, received in 1989 from Case Western Reserve University;

That, from 1987 until the present time he has been employed by the National Aeronautics and Space Administration as a Research Engineer at their Lewis Research Center, working exclusively in the area of high temperature materials and that his present position with them is Senior Research Engineer;

That, he is the sole author or a co-author of approximately fifty scientific publications in

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*Kent N. Stone*  
Kent N. Stone

the area of High Temperature Tribology and is a member of the Society of Tribologists and Lubrication Engineers (STLE) and the American Society of Mechanical Engineers (ASME);

That, he is familiar with the prosecution of the above-identified application and has studied and understands the Final Office Action and the two "Toyota" references cited in the Final Rejection, which references are titled *Development of Solid Lubricants for High Temperature Rolling Ceramic Bearings (Part 1): Various Solid Lubricants Based on Fluoride Compounds* and *Development of Solid Lubricants for High Temperature Rolling Ceramic Bearings (Part 2): Ternary System Solid Lubricants Composed of  $\text{CaF}_2 + \text{BaF}_2$  and  $\text{Cr}_2\text{O}_3$* ;

That, in order to make a direct comparison of the compositions of the invention and those disclosed in the two Toyota references, he calculated the volume percent compositions of the compositions of the invention and of the lubricant coatings disclosed in Table 1 of the Toyota Part 1 reference and in Table 1 of the Toyota Part 2 reference according to the following procedure, the results of which are summarized below;

#### PROCEDURE

The following sample calculations of a representative composition illustrate the calculation procedure used.

For PS300 in Table 2 on page 8 of the application

Constituent	wt. %	density (g/cc)	wt. (g) in 1 g sample	vol. (cc) in 1 g sample	vol. %
NiCr	20	8.56	0.2	0.0234	13.6
$\text{Cr}_2\text{O}_3$	60	5.2	0.6	0.115	67.1
Ag	10	10.5	0.1	0.009524	5.6
$\text{BaF}_2/\text{CaF}_2$	10	4.24	0.1	0.0236	13.7

Step 1 Calculate the weight of each constituent in a one gram sample.

NiCr	20 wt. % x 1 g = 0.2 g
Cr <sub>2</sub> O <sub>3</sub>	60 wt. % x 1 g = 0.6 g
Ag	10 wt. % x 1 g = 0.1 g
BaF <sub>2</sub> /CaF <sub>2</sub>	10 wt. % x 1 g = 0.1 g

Step 2 Calculate the volume contribution of each constituent in a 1 gram Sample and add the volume contributions to get the volume of one gram of the total composition.

NiCr	0.2 g ÷ 8.56 g/cc = 0.0234 cc
Cr <sub>2</sub> O <sub>3</sub>	0.6 g ÷ 5.2 g/cc = 0.115 cc
Ag	0.1 g ÷ 10.5 g/cc = 0.009524 cc
BaF <sub>2</sub> /CaF <sub>2</sub>	0.1 g ÷ 4.2 g/cc = <u>0.0236 cc</u>
Total	0.1715 cc

Step 3 Calculate the volume percent of each constituent in the composition

	vol. (cc) in 1 g sample	vol. (cc) of 1 g sample	vol. %
NiCr	0.0234	0.1715	13.6
Cr <sub>2</sub> O <sub>3</sub>	0.115	0.1715	67.1
Ag	0.009524	0.1715	5.6
BaF <sub>2</sub> /CaF <sub>2</sub>	0.0236	0.1715	13.7

Step 4 Break down fluoride eutectic into individual fluorides to be able to make more direct comparison to Toyota compositions.

	wt. %	Density g/cc	wt. (g) in 1 g sample	vol. (cc) in 1 g sample	vol. %
BaF <sub>2</sub>	62	4.89	0.62	0.127	51
CaF <sub>2</sub>	38	3.2	0.38	0.120	49

Note, in the compositions of the invention, the volume percent fluoride Breakdown is about ½ BaF<sub>2</sub> and ½ CaF<sub>2</sub>. However, by weight percent it is 62 % BaF<sub>2</sub> and 38 % CaF<sub>2</sub>. In the Toyota compositions it is 60 wt. % BaF<sub>2</sub> and 40 wt. % CaF<sub>2</sub> which is close to the 62/38 wt. % ratio of the compositions of the invention, and the volume % is about half and half.

## RESULTS

The results of the calculations are summarized and set forth in the Tables below.

Table 1  
Toyota Part 1 Table 1 Compositions in Volume %

	Constituent in volume percent				
Coating	NiCoCrAlY Binder*	Cr <sub>2</sub> O <sub>3</sub>	Ag	BaF <sub>2</sub>	CaF <sub>2</sub>
CB	80	0	0	10	10
CBA	80	0	5.6	7.2	7.2
CBCr	80	8.9	0	5.55	5.55
Cr	90	10	0	0	0
BCr	80	9.7	0	10.3	0
Bi	80	20**	0	0	0
CBCrA/3	80	7.5	3.5	4.5	4.5
CBCrA/4	80	8.4	2.6	5	5
CBCrBi	80	11.4***	0	4.3	4.3

\* Binder contains, by wt. %, 46.8 % Ni, 23.2 % Cr, 17 % Co, 12.5 % Al and 0.5 % Y

\*\* 20 vol. % Bi<sub>2</sub>O<sub>3</sub>

\*\*\* 11.4 vol. % made up of 7 % Cr<sub>2</sub>O<sub>3</sub> + 4.4 % Bi<sub>2</sub>O<sub>3</sub>

**Table 2**  
**Toyota Part 2 Table 1 Compositions in Volume %**

	Constituent in volume percent				
Test Piece No.	NiCoCrAlY Binder	Cr <sub>2</sub> O <sub>3</sub>	Ag	BaF <sub>2</sub>	CaF <sub>2</sub>
1	90	4.4	0	2.8	2.8
2	80	8.9	0	5.55	5.55
3	70	13.4	0	8.3	8.3
4	60	17.8	0	11.1	11.1
5	80	13.0	0	3.5	3.5
6	80	9.0	0	5.5	5.5

**Table 3**  
**Compositions of the Invention in Volume Percent**

Designation	NiCr Binder*	Cr <sub>2</sub> O <sub>3</sub>	Ag	BaF <sub>2</sub> **	CaF <sub>2</sub> **
PS 300	13.6	67.1	5.6	6.9	6.9
PS301	23.8	59.3	4.9	6.1	6.1
PS302	30.1	54.3	4.5	5.6	5.6
PS 303	35.6	50	4.2	5.1	5.1
PS304	49.5	27.2	6.7	8.3	8.3
PS305	49	33.6	5.0	6.2	6.2

\* NiCr by wt. % 80 Ni, 20 Cr; by vol. % 77 Ni, 23 Cr

\*\* BaF<sub>2</sub>/CaF<sub>2</sub> is 50/50 vol. % and 62/38 wt. %

Table 4  
Compositions of the Invention in Volume and Weight () Percent

Designation	NiCr Binder*	Cr <sub>2</sub> O <sub>3</sub>	Ag	BaF <sub>2</sub> **	CaF <sub>2</sub> **
PS 300	13.6 (20)	67.1 (60)	5.6 (10)	6.9 (6.2)	6.9 (3.8)
PS301	23.8 (33)	59.3 (50)	4.9 (8.3)	6.1 (5.1)	6.1 (3.2)
PS302	30.1 (40.7)	54.3 (44.5)	4.5 (7.4)	5.6 (4.6)	5.6 (2.8)
PS 303	35.6 (47)	50 (40)	4.2 (6.7)	5.1 (4.2)	5.1 (2.5)
PS304	49.5 (60)	27.2 (20)	6.7 (10)	8.3 (6.2)	8.3 (3.8)
PS305	49 (60)	33.6 (25)	5.0 (7.5)	6.2 (4.7)	6.2 (2.8)

\* NiCr by wt. % 80 Ni, 20 Cr; by vol. % 77 Ni, 23 Cr

\*\* BaF<sub>2</sub>/CaF<sub>2</sub> is 50/50 vol. % and 62/38 wt. %

Table 5  
Comparison of Major Constituent Volume % Ranges  
of Invention and Toyota Compositions

Compositions	Binder Metal	Cr <sub>2</sub> O <sub>3</sub>
Invention	13.6 to 49.5	27.2 to 67.1
Toyota	60 to 90	4.4 to 17.8

## CONCLUSIONS

That, the above composition Tables demonstrate that there is no overlap in ranges of the major constituents, which are the binder metal and the Cr<sub>2</sub>O<sub>3</sub>, between the Toyota compositions and the compositions claimed in the invention. The compositions claimed in the invention

include a metal binder in the range of 13.6 to 49.5 volume % (20 - 60 wt. %) and chromium oxide in the range of from 27.2 to 67.1 volume % (20 - 60 wt. %). In contrast, in the Toyota compositions, the mount of metal binder ranges from 60 to 90 volume % and the  $\text{Cr}_2\text{O}_3$  ranges from 4.4 to 17.8 volume %.

Christopher DellaCorte declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further, that the statements were made with the knowledge that willful false statements and the like, so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.



Christopher DellaCorte

6/24/98  
Date

KHS:ec

# Metals Handbook®

TENTH EDITION

## Volume 1 Properties and Selection: Irons, Steels, and High-Performance Alloys

Prepared under the direction of the  
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# Wrought and P/M Superalloys

N.S. Stoloff, Rensselaer Polytechnic Institute

**SUPERALLOYS** are heat-resisting alloys based on nickel, nickel-iron, or cobalt that exhibit a combination of mechanical strength and resistance to surface degradation. Superalloys are primarily used in gas turbines, coal conversion plants, and chemical process industries, and for other specialized applications requiring heat and/or corrosion resistance. The modern high-performance aircraft (jet) engine could not operate without the major advances made in superalloy development over the past 50 years. A noteworthy feature of nickel-base alloys is their use in load-bearing applications at temperatures in excess of 80% of their incipient melting temperatures, a fraction that is higher than for any other class of engineering alloys.

This article focuses on the properties of conventional wrought superalloys based on nickel, iron, and cobalt, as well as, on the properties of alloys produced from powder. The powder metallurgy (P/M) category includes alloys that were originally developed as casting alloys; new alloy compositions developed specifically to benefit from powder processing; and oxide dispersion strengthened (ODS) alloys (particularly those produced by mechanical alloying). The ODS alloys based on nickel and iron have been commercialized, whereas those based on cobalt have not. Other types of superalloys are described in the articles "Polycrystalline Cast Superalloys" and "Directionally Solidified and Single-Crystal Superalloys" in this Volume.

Applications of superalloys are categorized below; the bulk of tonnage is used in gas turbines:

- *Aircraft gas turbines*: disks, combustion chambers, bolts, casings, shafts, exhaust systems, cascs, blades, vanes, burner cans, afterburners, thrust reversers
- *Steam turbine power plants*: bolts, blades, stack gas reheaters
- *Reciprocating engines*: turbochargers, exhaust valves, hot plugs, valve seat inserts
- *Metal processing*: hot-work tools and dies, casting dies
- *Medical applications*: dentistry uses, prosthetic devices

- *Space vehicles*: aerodynamically heated skins, rocket engine parts
- *Heat-treating equipment*: trays, fixtures, conveyor belts, baskets, fans, furnace mufflers
- *Nuclear power systems*: control rod drive mechanisms, valve stems, springs, ducting
- *Chemical and petrochemical industries*: bolts, fans, valves, reaction vessels, piping, pumps
- *Pollution control equipment*: scrubbers
- *Metals processing mills*: ovens, afterburners, exhaust fans
- *Coal gasification and liquefaction systems*: heat exchangers, reheaters, piping

Many technical considerations, such as formability, strength, creep resistance, fatigue strength, and surface stability, must be evaluated when selecting a superalloy for any of the applications identified above. Unfortunately, those compositional and microstructural variables that benefit one property may result in undesirable performance in another area. For example, fine grain size is desirable for low-temperature tensile strength, fatigue crack initiation resistance, and high-temperature formability, but creep resistance is usually adversely affected. Similarly, high chromium contents in nickel alloys improve the resistance to oxidation and hot corrosion, but result in lower tensile and creep strengths and promote the formation of  $\sigma$  phase. Further, the more temperature resistant the alloy, the more likely it is to be segregation prone and, perhaps, brittle, and thus formable only by casting to shape or by using powder processing. For these and other compelling reasons, the interplay between composition, microstructure, consolidation method, mechanical properties, and surface stability is emphasized in this article.

## Wrought Nickel Alloys

Nickel alloys in commercial service and under development range from single-phase alloys to precipitation-hardened superalloys and oxide dispersion strengthened alloys and composites, the latter of which is de-

scribed in the section "P/M Alloys" in this article. Nickel-base superalloys are the most complex, the most widely used for the hottest parts, and, to many metallurgists, the most interesting of all superalloys. They currently constitute over 50% of the weight of advanced aircraft engines. Their use in cast form extends to the highest homologous temperature of any common alloy system (see the article "Polycrystalline Cast Superalloys" in this Volume).

The principal characteristics of nickel as an alloy base are the high phase stability of the face-centered cubic (fcc) nickel matrix and the capability to be strengthened by a variety of direct and indirect means. Further, the surface stability of nickel is readily improved by alloying with chromium and/or aluminum. In order to adequately describe mechanical behavior, however, it is first necessary to consider the composition and microstructure of the various classes of nickel alloys.

## Chemical Composition

The compositions of many representative nickel-base wrought alloys are listed in Table I. They can be categorized as nickel-iron-base alloys, in which nickel is the major solute element, or nickel-base, in which at least 50% Ni is present. The nickel-iron alloys are discussed in detail in a later section. The nickel-base superalloys discussed below are considered to be complex because they incorporate as many as a dozen elements. In addition, deleterious elements such as silicon, phosphorus, sulfur, oxygen, and nitrogen must be controlled through appropriate melting practices. Other trace elements, such as selenium, bismuth, and lead, must be held to very small (ppm) levels in critical parts.

Many wrought nickel-base superalloys contain 10 to 20% Cr, up to about 8% Al and Ti combined, 5 to 15% Co, and small amounts of boron, zirconium, magnesium, and carbon. Other common additions are molybdenum, niobium, and tungsten, all of which play dual roles as strengthening solutes and carbide formers. Chromium and aluminum are also necessary to improve surface stability through the formation of

Table 1 Nominal compositions of wrought nickel-base alloys

Alloy	Composition, %															
	Ni	Cr	Co	Mo	W	Nb	Al	Ti	Fe	Mn	Si	C	B	Zr	Other	
Astroloy	55.0	15.0	17.0	5.3	...	...	4.0	3.5	...	...	...	0.06	0.030	...	...	
Cabot 214	75.0	16.0	...	...	...	...	4.5	...	2.5	...	...	...	...	...	0.01 Y	
D-979	45.0	15.0	...	4.0	...	...	1.0	3.0	27.0	0.3	0.2	0.05	0.010	...	...	
Hastelloy C-22	51.6	21.5	2.5	13.5	4.0	...	...	...	5.5	1.0	0.1	0.01	...	...	0.3 V	
Hastelloy C-276	...	15.5	2.5	16.0	3.7	...	...	...	5.5	1.0	0.1	0.01	...	...	0.3 V	
Hastelloy G-30	42.7	29.5	2.0	5.5	2.5	0.8	...	...	15.0	1.0	1.0	0.03	...	...	2.0 Cu	
Hastelloy S	67.0	15.5	...	14.5	...	...	0.3	...	1.0	0.5	0.4	...	0.009	...	0.05 La	
Hastelloy X	47.0	22.0	1.5	9.0	0.6	...	...	...	18.5	0.5	0.5	0.10	...	...	...	
Haynes 230	57.0	22.0	...	2.0	14.0	...	0.3	...	...	0.5	0.4	0.10	...	...	0.02 La	
Inconel 587(a)	bal	28.5	20.0	...	...	0.7	1.2	2.3	...	...	...	0.05	0.003	0.05	...	
Inconel 597(a)	bal	24.5	20.0	1.5	...	1.0	1.5	3.0	...	...	...	0.05	0.012	0.05	0.02 Mg	
Inconel 600	76.0	15.5	...	...	...	...	...	...	8.0	0.5	0.2	0.08	...	...	...	
Inconel 601	60.5	23.0	...	...	...	...	1.4	...	14.1	0.5	0.2	0.05	...	...	...	
Inconel 617	54.0	22.0	12.5	9.0	...	...	1.0	0.3	...	...	...	0.07	...	...	...	
Inconel 625	61.0	21.5	...	9.0	...	3.6	0.2	0.2	2.5	0.2	0.2	0.05	...	...	...	
Inconel 706	41.5	16.0	...	...	...	2.9	0.2	1.8	40.0	0.2	0.2	0.03	...	...	...	
Inconel 718	52.5	19.0	...	3.0	...	5.1	0.5	0.9	18.5	0.2	0.2	0.04	...	...	...	
Inconel X750	73.0	15.5	...	...	...	1.0	0.7	2.5	7.0	0.5	0.2	0.04	...	...	...	
M-252	55.0	20.0	10.0	10.0	...	...	1.0	2.6	...	0.5	0.5	0.15	0.005	...	...	
Nimonic 75	76.0	19.5	...	...	...	...	...	0.4	3.0	0.3	0.3	0.10	...	...	...	
Nimonic 80A	76.0	19.5	...	...	...	...	1.4	2.4	...	0.3	0.3	0.06	0.003	0.06	...	
Nimonic 90	59.0	19.5	16.5	...	...	...	1.5	2.5	...	0.3	0.3	0.07	0.003	0.06	...	
Nimonic 105	53.0	15.0	20.0	5.0	...	...	4.7	1.2	...	0.3	0.3	0.13	0.005	0.10	...	
Nimonic 115	60.0	14.3	13.2	...	...	...	4.9	3.7	...	...	...	0.15	0.160	0.04	...	
Nimonic 263	51.0	20.0	20.0	5.9	...	...	0.5	2.1	...	0.4	0.3	0.08	0.001	0.02	...	
Nimonic 942(a)	bal	12.5	...	6.0	...	...	0.6	3.7	37	0.2	0.30	0.03	0.010	...	...	
Nimonic PE-11(a)	bal	18.0	...	5.2	...	...	0.8	2.3	35	0.20	0.30	0.05	0.03	0.2	...	
Nimonic PE-16	43.0	16.5	1.0	1.1	...	...	1.2	1.2	33.0	0.1	0.1	0.05	0.020	...	...	
Nimonic PK-33	56.0	18.5	14.0	7.0	...	...	2.0	2.0	0.3	0.1	0.1	0.05	0.030	...	...	
Pyromet 860	43	12.6	4.0	6.0	...	...	1.25	3.0	30.0	0.05	0.05	0.05	0.010	...	...	
René 41	55.0	19.0	11.0	1.0	...	...	1.5	3.1	...	...	...	0.09	0.005	...	...	
René 95	61.0	14.0	8.0	3.5	3.5	3.5	3.5	2.5	...	...	...	0.15	0.010	0.05	...	
Udimet 400(a)	bal	17.5	14.0	4.0	...	0.5	1.5	2.5	...	...	...	0.06	0.008	0.06	...	
Udimet 500	54.0	18.0	18.5	4.0	...	...	2.9	2.9	...	...	...	0.08	0.006	0.05	...	
Udimet 520	57.0	19.0	12.0	6.0	1.0	...	2.0	3.0	...	...	...	0.05	0.005	...	...	
Udimet 630(a)	bal	18.0	...	3.0	3.0	6.5	0.5	1.0	18.0	...	...	0.03	...	...	...	
Udimet 700	53.0	15.0	17.0	5.0	...	...	4.0	3.5	...	...	...	0.06	0.030	...	...	
Udimet 710	55.0	18.0	15.0	3.0	1.5	...	2.5	5.0	...	...	...	0.07	0.020	...	...	
Udimet 720	55.0	17.9	14.7	3.0	1.3	...	2.5	5.0	...	...	...	0.03	0.033	0.03	...	
Unitemp AF2-1DA6	60.0	12.0	10.0	2.7	6.5	...	4.0	2.8	...	...	...	0.04	0.015	0.10	1.5 Ta	
Waspaloy	58.0	19.5	13.5	4.3	...	...	1.3	3.0	...	...	...	0.08	0.006	...	...	

(a) Ref 2 (1984 data). Bal, balance. Source: Ref 1

Table 2 Role of elements in superalloys

Effect	Iron base	Cobalt base	Nickel base
Solid-solution strengtheners	Cr, Mo	Nb, Cr, Mo, Ni, W, Ta	Co, Cr, Fe, Mo, W, Ta
Fcc matrix stabilizers	C, W, Ni	Ni	...
Carbide form			
MC type	Ti	Ti, Ta, Nb	W, Ta, Ti, Mo, Nb
M <sub>2</sub> C <sub>3</sub> type	...	Cr	Cr
M <sub>23</sub> C <sub>6</sub> type	Cr	Cr	Cr, Mo, W
M <sub>6</sub> C type	Mo	Mo, W	Mo, W
Carbonitrides			
M(CN) type	C, N	C, N	C, N
Forms $\gamma'$ (Ni <sub>3</sub> Al, Ti)	Al, Ni, Ti	...	Al, Ti
Retards formation of hexagonal $\eta$ (Ni <sub>3</sub> Ti)	Al, Zr	...	...
Raises solvus temperature of $\gamma'$	...	...	Co
Hardening precipitates and/or intermetallics	Al, Ti, Nb	Al, Mo, Ti(a), W, Ta	Al, Ti, Nb
Forms $\gamma''$ (Ni <sub>3</sub> Nb)	...	...	Nb
Oxidation resistance	Cr	Al, Cr	Al, Cr
Improves hot corrosion resistance	La, Y	La, Y, Th	La, Th
Sulfidation resistance	Cr	Cr	Cr
Increases rupture ductility	B	B, Zr	B(b), Zr
Causes grain-boundary segregation	...	...	B, C, Zr
Facilitates working	...	Ni <sub>3</sub> Ti	...

(a) Hardening by precipitation of Ni<sub>3</sub>Ti also occurs if sufficient Ni is present. (b) If present in large amounts, borides are formed. Source: Ref 1

## Microstructure

The major phases that may be present in nickel-base alloys are:

- **Gamma matrix,  $\gamma$** , in which the continuous matrix is an fcc nickel-base nonmagnetic phase that usually contains a high percentage of solid-solution elements such as cobalt, iron, chromium, molybdenum, and tungsten. All nickel-base alloys contain this phase as the matrix.
- **Gamma prime,  $\gamma'$** , in which aluminum and titanium are added in amounts required to precipitate fcc  $\gamma'$  (Ni<sub>3</sub>Al, Ti), which precipitates coherently with the austenitic gamma matrix. Other elements, notably niobium, tantalum, and chromium, also enter  $\gamma'$ . This phase is required for high-temperature strength and creep resistance.
- **Gamma double prime,  $\gamma''$** , in which nickel and niobium combine in the presence of iron to form body-centered tetragonal (bct) Ni<sub>3</sub>Nb, which is coherent with the gamma matrix, while inducing large mismatch strains of the order of 2.9%. This phase provides very high strength at low

service, often in corrosive environments (refer to the Hastelloy-series and Inconel 600 shown in Table 1), are likely to contain chromium, molybdenum, iron, or tungsten in solution, with little or no second phase present.

# Polycrystalline Cast Superalloys

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**SUPERALLOYS** are a group of nickel-, iron-nickel-, and cobalt-base materials that exhibit outstanding strength and surface stability at temperatures up to 85% of their melting points ( $0.85 T_M$ ). They are generally used at temperatures above  $540^\circ\text{C}$  ( $1000^\circ\text{F}$ ). Superalloys were initially developed for use in aircraft piston engine turbosuperchargers, and their development over the past 50 years has been paced by the demands of advancing gas turbine engine technology.

The initial cast superalloy developments in the United States centered on cobalt-base materials. Cast Vitallium (Co-27Cr-5.5Mo-0.5Ni-0.25C) turbosupercharger blades were produced by the Austenal Company in 1942 in response to an overloaded forging industry and forgeability problems experienced with the early nickel-chromium-iron solid-solution wrought superalloys. This work ultimately led to the successful manufacture of investment cast components for the first U.S. production gas turbine engine in 1945 (Ref 1).

Nickel-base and nickel-iron-base superalloys owe their high-temperature strength potential to their gamma prime ( $\gamma'$ ) (Ni<sub>3</sub>Al,Ti) content. The first reference to aluminum or

titanium additions to the 80-20 Ni-Cr system occurred in a patent filed by Heraeus Vacuumschmelze A.G. in 1926, in which as much as 6% Al was added to a nickel-chromium alloy for increased tensile yield strength. Not until later in the decade, however, did a French patent application recognize the occurrence of precipitation hardening in nickel-chromium alloys. In 1929, Pilling and Merica concurrently filed a number of patent applications in the United States for precipitation-hardening nickel-base alloys containing aluminum and titanium, and in 1931 the first British patent applications covering aluminum plus titanium additions to nickel-base alloys were filed.

Although age hardening was recognized, it was not until the development of the Whittle engine in Great Britain, along with gas turbine engine developments in Germany, that material creep strength was a recognized consideration. The requirement for creep resistance led to an understanding of the relationship between age hardening and creep, eventually pacing the rate of development of  $\gamma'$ -strengthened nickel-base alloys.

The first commercial nickel-base alloy developmental work, undertaken by the

British in the early 1940s, led to the wrought Nimonic 75 and 80 alloys. Increased operating-temperature requirements for U.S. aircraft engines resulted in the use of aluminum plus titanium strengthened wrought materials during the same period of time. Component forgeability problems, however, led to the use of cast Vitallium until the shortages of cobalt supply experienced during the Korean War caused further research on nickel-base alloys.

Cast nickel-base alloy developments outpaced cobalt-base developmental work by the late 1950s because of their superior strengthening potential, that is, stable, coherent intermetallic compound  $\gamma'$  phase introduction. The introduction of commercial vacuum induction melting (VIM) and vacuum investment casting in the early 1950s provided further potential for  $\gamma'$  exploitation. Many nickel-base alloy developments resulted, continuing through the 1960s (Fig. 1). The compositions of cast nickel- and cobalt-base superalloys are listed in Tables 1 and 2, respectively; Tables 3 to 6 list physical and mechanical properties of cast nickel- and cobalt-base superalloys.

The development of new polycrystalline alloys continued through the 1970s, howev-

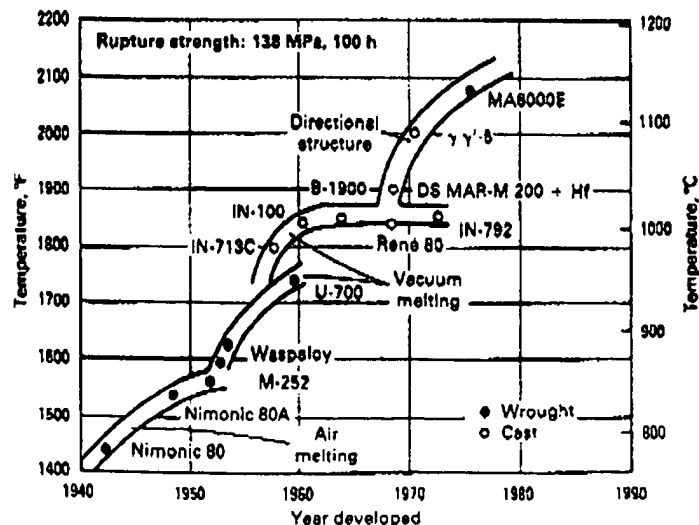


Fig. 1 Progress in the high-temperature capabilities of superalloys since the 1940s. Source: Ref 2

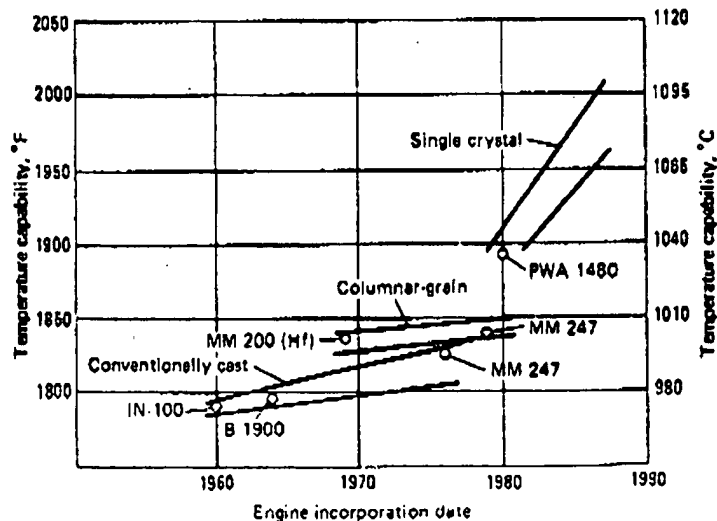


Fig. 2 Advances in turbine blade materials and processes since 1960. Source: Ref 4

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## Nominal composition of selected cast nickel-base superalloys

Alloy	Composition, %													Other	Density, g/cm <sup>3</sup>
	C	Cr	Co	Mo	W	Ta	Nb	Al	Ti	Hf	Zr	B	Ni		
IN-718	0.04	18.5	...	3.0	...	...	5.1	0.5	0.9	...	...	...	bal	18.5 Fe	8.22
René 200	0.03	19.0	12.0	3.2	...	3.1	5.1	0.5	1.0	...	...	...	bal	...	...
IN-625	0.06	21.5	...	8.5	...	...	4.0	0.2	0.2	...	...	...	bal	2.5 Fe	...
IN-713C	0.12	12.5	...	4.2	...	...	2.0	6.1	0.8	...	0.10	0.012	bal	...	8.24
IN-713LC	0.05	12.0	...	4.3	...	...	2.0	5.9	0.6	...	0.10	0.01	bal	...	8.00
IN-713 Hf (MM 004)	0.05	12.0	...	4.3	...	...	2.0	5.9	0.6	1.3	0.10	0.01	bal	...	...
IN-100	0.18	10.0	15.0	3.0	...	...	...	5.5	4.7	...	0.06	0.014	bal	1.0 V	7.75
IN-738C	0.17	16.0	8.5	1.75	2.6	1.75	0.9	3.4	3.4	...	0.10	0.01	bal	...	8.11
IN-738LC	0.11	16.0	8.5	1.75	2.6	1.75	0.9	3.4	3.4	...	0.04	0.01	bal	...	...
IN-792	0.21	12.7	9.0	2.0	3.9	3.9	...	3.2	4.2	...	0.10	0.02	bal	...	8.25
IN-939	0.15	22.4	19.0	...	2.0	1.4	1.0	1.9	3.7	...	0.10	0.009	bal	...	8.2
B-1900	0.10	8.0	10.0	6.0	...	4.3	...	6.0	1.0	...	0.08	0.015	bal	...	8.2
B-1900 Hf (MM 007)	0.10	8.0	10.0	6.0	...	4.3	...	6.0	1.0	1.5	0.08	0.015	bal	...	8.25
B-1910	0.10	10.0	10.0	3.0	...	7.0	...	6.0	1.0	...	0.10	0.015	bal	...	...
MM 002	0.15	9.0	10.0	...	...	2.5	...	5.5	1.5	1.5	0.05	0.015	bal	...	...
MAR-M 200	0.15	9.0	10.0	...	12.5	...	1.8	5.0	2.0	...	0.05	0.015	bal	...	8.53
MAR-M 200 Hf (MM 009)	0.14	9.0	10.0	...	12.5	...	1.0	5.0	2.0	2.0	...	0.015	bal	...	...
MAR-M 246	0.15	9.0	10.0	2.5	10.0	1.5	...	5.5	1.5	...	0.05	0.015	bal	...	8.44
MAR-M 246 Hf (MM 006)	0.15	9.0	10.0	2.5	10.0	1.5	...	5.5	1.5	1.4	0.05	0.015	bal	...	...
MAR-M 247 (MM 0011)	0.16	8.5	10.0	0.65	10.0	3.0	...	5.6	1.0	1.4	0.04	0.015	bal	...	8.53
CM 247LC	0.07	8.1	9.3	0.5	9.5	3.0	...	5.6	0.7	1.4	0.01	0.015	bal	...	...
René 41	0.08	19.0	10.5	9.5	...	...	...	1.7	3.2	...	0.01	0.005	bal	...	...
René 77	0.08	15.0	18.5	5.2	...	...	...	4.25	3.5	...	...	0.015	bal	...	7.91
René 80	0.17	14.0	9.5	4.0	4.0	...	...	3.0	5.0	...	0.03	0.015	bal	...	8.16
René 80 Hf	0.15	14.0	9.5	4.0	4.0	...	...	3.0	4.7	0.8	0.01	0.015	bal	...	...
René 100	0.15	9.5	15.0	3.0	...	...	...	5.5	4.2	...	0.06	0.015	bal	1.0 V	7.75
René 125 Hf (MM 005)	0.10	9.0	10.0	2.0	7.0	3.8	...	4.8	2.6	1.6	0.05	0.015	bal	...	...
Nimocast 75	0.12	20.0	...	...	...	...	...	...	0.5	...	...	...	bal	...	8.44
Nimocast 80	0.05	19.5	...	...	...	...	...	1.4	2.3	...	...	...	bal	1.5 Fe	8.17
Nimocast 90	0.06	19.5	18.0	...	...	...	...	1.4	2.4	...	...	...	bal	1.5 Fe	8.18
Nimocast 95	0.07	19.5	18.0	...	...	...	...	2.0	2.9	...	0.02	0.015	bal	...	...
Nimocast 100	0.20	11.0	20.0	5.0	...	...	...	5.0	1.5	...	0.03	0.015	bal	...	...
Udimet 500	0.08	18.5	16.5	3.5	...	...	...	3.0	3.0	...	...	0.006	bal	...	8.02
Udimet 700	0.08	14.3	14.3	4.3	...	...	...	4.25	3.5	...	0.02	0.015	bal	...	...
Udimet 710	0.13	18.0	15.0	3.0	1.5	...	...	2.5	5.0	...	0.08	...	bal	...	8.08
C 130	0.04	21.5	...	10.0	...	...	...	0.8	2.6	...	...	...	bal	...	...
C 242	0.30	20.0	10.0	10.3	...	...	...	0.1	0.2	...	...	...	bal	...	...
C 263	0.06	20.0	20.0	5.9	...	...	...	0.45	2.15	...	0.02	0.001	bal	...	...
C 1023	0.15	15.5	10.0	8.0	...	...	...	4.2	3.6	...	...	0.006	bal	...	...
Hastelloy X	0.08	21.8	1.5	9.0	0.6	...	...	...	...	...	...	...	bal	18.5 Fe, 0.5 Mn, 0.3 Si	...
Hastelloy S	0.01	16.0	...	15.0	...	...	...	0.40	...	...	...	0.009	bal	3.0 Fe, 0.02 La, 0.65 Si, 0.35 Mn	...
Waspaloy	0.06	19.0	12.3	3.8	...	...	...	1.2	3.0	...	0.01	0.005	bal	0.45 Mn	...
NX 188	0.04	...	...	18.0	...	...	...	8.0	...	...	...	...	bal	...	...
SEL	0.08	15.0	26.0	4.5	...	...	...	4.4	2.4	...	...	0.015	bal	...	...
CMSX-2(a)	...	8.0	4.6	0.6	8.0	6.0	...	5.6	1.0	...	...	...	bal	...	8.6
GMR-235	0.15	15.0	...	4.8	...	...	...	3.8	2.0	...	...	0.05	bal	0.3 Mn, 0.4 Si, 11.0 Fe	8.0
CMSX-3(a)	...	8.0	4.6	0.6	8.0	6.0	...	5.6	1.0	0.10	...	...	bal	...	8.6
CMSX-4(a)	...	6.4	9.6	0.6	6.4	6.5	...	5.6	1.0	0.10	...	...	bal	3.0 Re	8.7
CMSX-6(a)	...	9.9	5.0	3.0	...	2.0	...	4.8	4.7	0.05	...	...	bal	...	7.98
GMR-235	0.15	15.0	...	4.8	...	...	...	3.5	2.5	...	...	0.05	bal	4.5 Fe	8.04
SEL-15	0.07	11.0	14.5	6.5	1.5	...	0.5	5.4	2.5	...	...	0.015	bal	...	8.7
UDM 56	0.02	16.0	5.0	1.5	6.0	...	...	4.5	2.0	...	0.03	0.070	bal	0.5 V	8.2
M-22	0.13	5.7	...	2.0	11.0	3.0	...	6.3	...	...	0.60	...	bal	...	8.63
IN-731	0.18	9.5	10.0	2.5	...	...	...	5.5	4.6	...	0.06	0.015	bal	1.0 V	7.75
MAR-M 421	0.14	15.8	9.5	2.0	3.8	...	...	4.3	1.8	...	0.05	0.015	bal	...	8.08
MAR-M 432	0.15	15.5	20.0	...	3.0	2.0	2.0	2.8	4.3	...	0.05	0.015	bal	...	8.16
MC-102	0.04	20.0	...	6.0	2.5	0.6	6.0	...	...	...	...	...	bal	0.25 Si, 0.30 Mn	...
Nimocast 242	0.34	20.5	10.0	10.5	...	...	...	0.2	0.3	...	...	...	bal	1.0 Fe, 0.3 Mn, 0.3 Si	8.40
Nimocast 263	0.06	20.0	20.0	5.8	...	...	...	0.5	2.2	...	0.04	0.008	bal	0.5 Fe, 0.5 Mn	8.36

(a) Single crystal

er, at a more moderate rate. Attention was concentrated instead on process development, with specific interest directed toward grain orientation and directional-solidification (DS) turbine blade and vane casting technology (Fig. 2).

Applied to turbine blades and vanes, the DS casting process results in the alignment of all component grain boundaries such that they are parallel to the blade/vane stacking fault axis, essentially eliminating transverse grain boundaries (Fig. 3). Because turbine

blades/vanes encounter major operating stress in the direction which is near normal to the stacking fault axis, transverse grain boundaries provide relatively easy fracture paths. The elimination of these paths provides increased strain elasticity by virtue of the lower (001) elastic modulus, thereby creating opportunities for further exploitation of the nickel-base alloy potential.

The logical progression to grain-boundary reduction is the total elimination thereof. Thus, single-crystal turbine blade/vane

casting technology soon developed, providing further opportunity for nickel-base alloy design innovation.

The late 1970s and the 1980s have, therefore, been a productive development period for nickel-base alloys designed specifically for directionally solidified columnar-grain and single-crystal cast components. These new process technologies, which are more fully discussed in the article "Directionally Solidified and Single-Crystal Superalloys" in this Volume, have contributed to dramat-